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Water Pollution Reduction Through Recovery of Desizing Wastes

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Processes for precipitating from desizing wastes the synthetic warp sizes, carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA), were investigated. Carboxymethyl cellulose is precipitated quantitatively by certain multivalent metal salts, such as aluminum sulfate and ferric chloride. Aluminum sulfate is the more suitable for size recovery. Cycles of sizing, desizing and size recovery were performed on cottonpolyester (65:35) yarns, starting with commercial CMC, and continuing with only the recovered material. After four cycles, the performance of the recovered CMC on a Callaway slasher was satisfactory and results with the sized yarns on a warpshed tester were equivalent to results with yarns sized with new CMC. Two copolymers of PVA were prepared, one of which was precipitated from dilute solution by aluminum sulfate and ferric chloride, the other by acidification. Preliminary sizing trials with small samples of materials indicate that these, or similar, copolymers may be effective, recoverable warp sizes. Evidence was obtained that acclimatization of sewage bacteria to CMC and PVA occurs upon prolonged contact in a laboratory activated-sludge unit. (Lowry, Texas)

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WATER POLLUTION REDUCTION
THROUGH
RECOVERY OF DESIZING WASTES

by

DEPARTMENT OF TEXTILE CHEMISTRY
SCHOOL OF TEXTILES
NORTH CAROLINA STATE UNIVERSITY
RALEIGH, NORTH CAROLINA 27607

for the

ENVIRONMENTAL PROTECTION AGENCY
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January 1972

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ABSTRACT

Processes for precipitating from desizing wastes the synthetic warp sizes, carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA), were investigated. Carboxymethyl cellulose is precipitated quantitatively by certain multivalent metal salts, such as aluminum sulfate and ferric chloride. Aluminum sulfate is the more suitable for size recovery.

Cycles of sizing, desizing and size recovery were performed on cotton-polyester (65:35) yarns, starting with commercial CMC, and continuing with only the recovered material. After four cycles, the performance of the recovered CMC on a Callaway slasher was satisfactory and results with the sized yarns on a warp-shed tester were equivalent to results with yarns sized with new CMC.

Two copolymers of PVA were prepared, one of which was precipitated from dilute solution by aluminum sulfate and ferric chloride, the other by acidification. Preliminary sizing trials with small samples of materials indicate that these, or similar, copolymers may be effective, recoverable warp sizes.

Evidence was obtained that acclimatization of sewage bacteria to CMC and PVA occurs upon prolonged contact in a laboratory activated-sludge unit.

This report was submitted in fulfillment of Project 12090 EOE under the sponsorship of the Water Quality Office, Environmental Protection Agency.

Key words: acclimatization, alum, carboxymethyl cellulose, industrial wastes, pollution abatement, polyvinyl alcohol, precipitation, reuse, textiles, warp sizes.

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SECTION I

CONCLUSIONS

1. A process for recovering carboxymethyl cellulose (CMC) from desizing wastes by precipitation with aluminum sulfate (filter alum) has been developed on a laboratory scale. Considerable testing indicates that the process may have practical applications. The recovered CMC may be suitable for reuse as a warp size; if not, it may be disposed of as a solid without further treatment.
2. A similar process for recovering a modified polyvinyl alcohol (PVA) from desizing wastes has been developed also, although it has not been tested as thoroughly as the CMC process.
3. An attractive procedure was not found for recovering the conventional warp-size-grade PVA from desizing wastes. Recovery of this material by precipitation, without a prior concentrating step, does not seem feasible.
4. Evidence was obtained that acclimatization of sewage bacteria to CMC and PVA occurs upon prolonged contact in a laboratory activated sludge unit. The synthetic sizes then exhibit biodegradable characteristics.
5. A precipitation method for recovering the desizing products of starch from desizing wastes was not found.
6. Examination of enzymatic desizing wastes, from starch-sized fabrics, obtained from a nearby textile plant, showed that none of the low-molecular-weight sugars was present. The starch was degraded to a more water-soluble material but the degradation was only partial, leaving products of molecular weights higher than those of the simple sugars.

SECTION II

RECOMMENDATIONS

1. The process for precipitating CMC from desizing wastes should be given further evaluation and development on a larger scale. A cooperative project, supported by a Demonstration Grant, using pilot-plant facilities located at an industrial plant, with supporting laboratory work at the University, is recommended.
2. In recovering CMC from desizing wastes, emphasis should be placed on obtaining material suitable for reuse as a warp size. Tests on the recovered material should be made to determine the extent to which reuse is possible.
3. The development of a process for the recovery from desizing wastes of a warp size based on a modified PVA should be continued. The contemplated method of recovery is similar to the coagulation and precipitation scheme that was successful with CMC. A satisfactory recovery procedure should be followed by tests on the recovered material to determine its suitability for reuse as a warp size.
4. Other processes for recovering warp sizes from desizing wastes should be investigated. It is important that eagerness to promote the processes for recovering CMC and PVA does not lead to overlooking other processes, possibly employing new warp-size modifications, which might turn out to be better. An example would be to employ as a warp size a polymer, such as methyl cellulose, which is soluble in water at room temperature but insoluble in hot water; the size would be applied and removed at room temperature and then precipitated and recovered from the desizing waste upon heating.
5. Because of the exceedingly large amount of starch used in sizing textile yarns, further exploratory work should be carried out on chemical and physical methods for removing the desizing products of starch from desizing wastes. Such methods should be compared with the usual biological processes for removing these products.

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SECTION III

INTRODUCTION

Background Information

Removal of the size with which the warp (length-wise) yarns are coated to make the weaving of the fabric possible is a common operation in the preparation of cloth for dyeing and finishing. The basis of most warp sizes for yarns of cellulose (cotton, rayon) and cellulose blends is starch and modified starches. These materials are biodegradable and, because they are used in relatively large quantities -- 5 to 15% of yarn weight, amounting to over 300,000,000 pounds annually in this country, contribute heavily (45-70% of total) to the biochemical oxygen demand (BOD-5) of textile finishing wastes.

In recent years certain water-soluble, synthetic polymers, with a much lower BOD-5 than starch, have been introduced for use as warp sizes. Of these materials, carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA) have gained the widest use. Although cost of these materials is higher than that of starch, (approximately 6¢/lb for starch, 8-18¢/lb for modified starches, 31¢/lb for PVA, and 35¢/lb for CMC, all in the unformulated state), they have certain advantages in performance, particularly with the synthetics and cotton-synthetic blends, which tend to offset this cost differential. The use of these compounds, therefore, can be expected to increase in the coming years as the use of synthetic fibers increases.

Besides giving increased operating efficiencies, the synthetic warp sizes, having a low BOD-5, have been promoted also as a means of reducing the pollution potential of desizing wastes. The chemical oxygen demand (COD) of CMC is about as high as that of starch, however, and the COD of PVA is higher. Furthermore, results already obtained in this laboratory as well as in others, indicate that adaptation of bacteria to carboxymethyl cellulose (9) and probably to polyvinyl alcohol (11) as well, does occur over a prolonged period of time.

Research to decrease the waste load from the desizing of fabrics, therefore, may be concerned with developing more effective and less expensive treatment methods or with developing processes for recovering and reusing the desizing products. The latter alternative appears to be the more desirable whenever it is possible and, indeed, to represent almost the ultimate in pollution control.

Recovery Methods.

The contemplated methods of recovering desizing products were precipitation, evaporation, and combinations of the two. Emphasis was placed on precipitation methods which do not require evaporation or other concentrating procedures because, for economic reasons, the process should be as simple as possible.

Two general methods may be considered for precipitating warp sizes from desizing wastes. In one method, the warp size is chosen, or modified chemically before application, so that it can be readily precipitated from dilute solution by a suitable precipitating agent. In the other method, the desizing wastes are treated in a manner to modify the warp size so that it may be readily precipitated.

The scheme for recovering carboxymethyl cellulose (CMC) is an example of the first method, which appears also to offer a good way for recovering polyvinyl alcohol (PVA).

The second method has provided the approach taken in attempts to develop a method for removal of conventional warp-size-grade PVA from desizing wastes because, without chemical modification, this PVA does not possess reactive sites which will permit it to be precipitated from dilute solution by a simple precipitating reaction. For the same reason, this approach was taken in attempts to develop a method for removal of the desizing products from starch-desizing wastes.

Scope and Purpose of Project

The scope and purpose of the project are defined by the objectives which were

- (a) to develop processes for the recovery of desizing wastes---from fabrics sized with carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), and starch---in forms suitable for final disposal;
- (b) to develop processes for the recovery of desizing wastes in a reusable form---with the recognition that reuse, as a size, of the desizing products from starch is not possible, since starch is degraded during desizing;
- (c) to obtain more complete data on the biodegradation of the synthetic warp sizes, CMC and PVA, thus gaining information on the fate of these materials in biological treatment systems and in streams.

The experiments carried out to attain these objectives were limited to the laboratories and pilot plant of the Department of Textile Chemistry, North Carolina State University.

SECTION IV

STUDIES AND DISCUSSION

Recovery and Reuse of Carboxymethyl Cellulose (CMC)

The literature states that sodium carboxymethyl cellulose (CMC) may be precipitated as an insoluble salt of aluminum, copper, lead, uranium or zirconium (6) . Early work on this project established that an almost quantitative recovery of warp-size-grade CMC can be obtained by precipitation from a 0.1% solution with aluminum sulfate (filter alum) . The recovered material, which retained a small amount of aluminum, appeared to be suitable for solid disposal after dewatering. On the other hand, the CMC, precipitated with alum, dissolved in dilute sodium hydroxide and was found suitable for further use as a sizing agent for cotton yarn. Performance of the recovered CMC on the Callaway slasher, a laboratory sizing machine, was satisfactory and the results obtained with the sized yarns on a warp shed tester, which simulates loom performance, were comparable to those obtained with yarns sized with new CMC.

Chemical equations for the conversion of CMC (warp-size-grade) to the water-insoluble aluminum carboxymethyl cellulose and for the reaction of the latter with sodium hydroxide to give a solution of CMC again are shown in Figure 1.

Data on precipitation of CMC from 0.1% solution with filter alum are shown in Table 1. A ratio of alum to CMC of 0.71 is enough to form the aluminum salt of CMC but a larger ratio is necessary to give rapid coagulation and precipitation and to form a clear supernatant. The leveling of recovery at 96% of the original weight occurs because commercial, warp-size-grade CMC contains about 4% sodium chloride, a by-product in its manufacture, which is not precipitated by alum. The increase in total solids in the supernatant with increasing alum-CMC ratios reflects the increasing amounts of excess alum which remain in solution.

A series of cycles of sizing, desizing, and size recovery was carried out, starting with fresh, commercial, warp-size-grade CMC and, in subsequent operations, continuing with only the material recovered from the previous step. The sizing trials were carried out on a blended yarn of cotton and polyester (65:35) with an add-on of size of approximately ten percent of yarn weight. Wax, ten percent based on size, was added to the initial size bath only; apparently it is recovered along with the CMC upon precipitation with alum. The scale of these operations is shown in Table 2. This table shows also the disproportionately high attrition, arising from mechanical losses, which occurs in working with relatively small amounts of materials. The preceding table shows that these losses did not occur because the precipitation and recovery of CMC was incomplete. Such losses, of course,

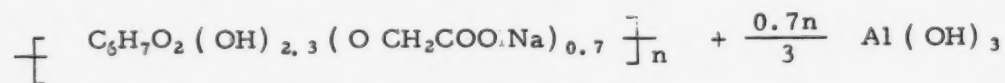


Figure 1. Chemical Equations for (a) Precipitation of CMC with Filter Alum and (b) Solution of the Precipitate with Sodium Hydroxide

Table 1: Recovery of CMC by Precipitation with Filter Alum
(from 0.1% solution of CMC)

Ratio by weight Alum/CMC	Precipitate Recovered (%)	Total Solids (wt %)	Supernatant Appearance
0.50	81	0.051	cloudy
0.75	95	0.065	slightly cloudy
1.00	96	0.085	clear
1.25	95	0.099	clear
1.50	96	0.127	clear
2.00	96	0.166	clear

Table 2: Sizing with CMC - New and Recovered
(Yarn: Cotton-polyester (65:35) blend)

Run No.	1	2	3	4	5
Reuse No.	1	2	3	4	
Sizing soln prepared (gal.)	10	5	2	0.4	
Concn. of sizing soln (wt %)	8-9	8-9	8-9	8-9	13
pH of sizing soln	7.3	8.0	7.5	7.3	8.0
Warp sized (yd)	6000	3600	1800	600	60
Solids in desizing liquor (wt %)	1.10	1.05	1.05	0.97	

would not be nearly as large proportionately in a large, plant operation.

After four cycles, the performance of the recovered CMC on the Callaway slasher was still satisfactory and the results obtained with the sized yarns on a warp-shed tester were equivalent to those obtained with yarns sized with new CMC (See Table 3). On the fifth cycle, however, the results on the warp-shed tester were slightly poorer in that the percent of shed was higher, the clinging was greater, and there were more stops. The poorer results might be due to an accumulation of impurities in the recovered CMC or they might be due to the method of application which was less easily controlled because of the small amount of recovered CMC remaining at this point.

The properties of the size at the several stages of recovery are shown in Table 4. In Runs 2 and 3, the CMC recovered from the previous run as a swollen floc was dried in an oven at 105°C and ground to a powder before dissolving for reuse; in Runs 4 and 5, the swollen floc was dissolved directly, eliminating the time and expense of two unnecessary steps. The continuous diminution in amount of recovered size because of mechanical losses was remarked on above. The decrease in CMC content of the recovered material and the increase in residues remaining at 600°C are undoubtedly due to a build-up of impurities. The high value for residues obtained for the new CMC is probably due largely to the presence of sodium chloride which is formed as a by-product in the manufacture of CMC. The aluminum content of the recovered material is apparently leveling off at about 4%, a value which does not appear excessive since the theoretical aluminum content of aluminum carboxymethyl cellulose is 3.0%.

The steady decrease in the total solids and the CMC content of the supernatant from the recovery of size (see Table 5) occurred undoubtedly because a larger amount of alum was added in the latter precipitations. The increase was made when it was realized that the rapid precipitation and settling, obtained with larger amounts of alum, would be required for a practical plant operation; the slight increase in the amount of material recovered is of secondary importance. The increase in the aluminum content of the supernatant from the latter recoveries also reflects this change.

The brown color of the recovered CMC showed that some of the natural impurities of the cotton component of the yarn, and probably the spinning oil used on the polyester component as well, are retained by the CMC during recovery, while the yellow or tan color of the liquor remaining indicates that some of these materials remain in solution. The performance tests mentioned above, however, indicate that these materials have no deleterious effects during four cycles of operations--and perhaps, longer--and the appearance of the yarns after desizing indicates that none is retained by the yarns.

Table 3: Results from Warp Shed Tester on Yarns Sized
with New and Recovered CMC

Run No.	1	2	3	4	5
Reuse No.	1	2	3	4	
Size add-on (wt%)	8.7	10.6	9.0	10.7	13.5
Shed (wt%)	3.1	2.7	2.7	2.7	3.3
Fiber in shed (wt%)	40	55	50	30	50
Stops	0	0	1	1	2
Clinging ratio (%)	50	25	50	25	50+
Warp tested (yd)	20	20	20	20	20

Table 4: Date on CMC Size Recovered by Precipitation

Run No.	1	2	3	4	5
Reuse No.	1	2	3	4	
Form when dissolved	dry powder	dry powder	dry powder	swollen floc	swollen floc
Dry weight (lb)		5.4	3.5	1.5	0.25
CMC content (%)		92	84	82	72
Aluminum content (%)	0	3.3	4.3	4.0	4.3
Residue at 600°C (%)	33	10.8	15.0	16.0	22.9

Table 5: Data on Supernatant from Precipitation
of CMC Size

Run No.	1	2	3	4
Reuse No.	1	2	3	
Solids (wt %)	0.6	0.6	0.5	0.4
CMC (wt %)	0.04	0.03	0.006	0.003
Aluminum content (ppm)	225	375	400	400
pH	4.0	3.9	3.7	3.8

The accumulation of impurities can be expected to reach harmful proportions eventually, however, and some of the recovered size will have to be discarded as a solid waste and replaced with fresh CMC. This exchange most probably should be made gradually, beginning with the first recovery, to an extent which permits attainment of steady-state conditions.

Material costs in the recovery of CMC from desizing wastes by precipitation with filter alum are favorable. The current prices of CMC is approximately 35 ¢/lb and that of filter alum 3 ¢/lb. Since approximately one pound, or less, of filter alum is used in the recovery of one pound of CMC, the material cost of recovery is somewhat less than 10% of that of the CMC recovered.

Carboxymethyl cellulose is precipitated also from dilute aqueous solution by ferric chloride but the floc is more voluminous and does not settle as well. The cost of ferric chloride is about 4 ¢/lb, somewhat higher than that of alum, but the stoichiometry is such that only about 80% as much is required for complete precipitation of CMC. Material costs of the two in the precipitation process, therefore would be about the same. Because of the retention of a small amount of iron in the precipitate and of the known adverse effect of iron during bleaching, however, this precipitant does not appear to be useful in recovering CMC intended for reuse. The presence of a small amount of aluminum in sizes recovered from desizing liquors by precipitation with alum does not appear to present any problem in size reuse.

The process for precipitating and recovering CMC from desizing wastes should be given evaluation and development on a larger scale. Emphasis should be placed on obtaining material suitable for reuse as a warp size. A cooperative project, supported by a Demonstration Grant, using the facilities at a textile-finishing plant, with supporting laboratory and pilot-plant work at the University, appears to be a preferred way of performing the further work required. A brief outline of this work is as follows.

1. Desizing of fabrics, sized with CMC, would be carried out at the textile-finishing plant, using equipment normally used in the industry. The fabrics would be supplied by the textile plant.
2. Equipment would be designed and constructed for precipitating and separating the CMC from the bulk of the desizing wastes. This equipment would be tried in the plant and modified if necessary.
3. The CMC, recovered in the form of a sludge, would be taken to the University and dewatered to the desired extent by centrifuging.
4. The dewatered CMC, still highly swollen with water, would be dissolved in sodium hydroxide to make a new desizing solution. Warp yarns would be sized on a Callaway slasher and tested on a warp-shed tester.
5. Chemical analysis would be made throughout the process of recovery and reuse to serve as a control and to guide in making improvements in subsequent trials.
6. Successful results in the preceding stages would be followed by weaving trials on full-scale looms at the University.

Recovery of Polyvinyl Alcohol (PVA) from Desizing Wastes

The work with polyvinyl alcohol (PVA) has not progressed as far as that with CMC. An attractive procedure was not found for precipitating and recovering the conventional warp-size-grade PVA from desizing wastes, although a number of materials that will insolubilize PVA are reported in the literature (1, 2, 10) . These materials are classified below according to the effect produced on PVA; there is some overlapping in the classification, however.

Precipitants. Polyvinyl alcohol is insoluble in solutions of many salts and can be precipitated from solution by addition of a salt such as sodium sulfate or sodium carbonate. Desizing wastes are so dilute, however, that the amount of salt required would be impractical and would create a pollution problem itself.

Insolubilizers. The water resistance of films and coatings of PVA can be increased by incorporating any of a number of insolubilizing agents. These agents include the amine- or amide-formaldehyde condensates, such as dimethylol urea, trimethylol melamine and the various compositions used to impart durable-press properties to cellulosic fabrics; aldehydes, such as formaldehyde, glyoxal, and hydroxyadipaldehyde; polyvalent metal salts and complexes, from such metals as aluminum, chromium, copper, iron, nickel, and titanium; and organic titanates. Insolubilization of PVA by these materials, however, is limited to dried films, usually with baking, and cannot be applied to aqueous solutions.

Gelling agents. A number of compounds can cause gellation of solutions of PVA in water. These compounds include certain dyes, such as Congo Red; phenolic compounds, such as resorcinol, catechol, phloroglucinol, gallic acid, salicylamide, and 2, 4 - dihydroxybenzoic acid; and inorganic complexing agents, such as borax--a particularly effective gelling agent, certain vanadates, and compounds of trivalent chromium and of tetravalent titanium. These compounds cause gellation only in PVA solutions in which the concentration of PVA is higher than that likely to be encountered in desizing wastes and, of course, gellation of the entire solution provides no means of separating the PVA.

Consideration of the literature cited above, together with qualitative experiments with borax, phenolic compounds, and aldehydes, led to the conclusion that precipitating and recovering conventional warp-size-grade PVA from desizing wastes, without a prior concentrating step, would be difficult if not impossible.

A modified PVA has been prepared which is precipitated from dilute solution by filter alum. This material was prepared by emulsion copolymerization of vinyl acetate with a relatively small amount of acrylic acid and hydrolysis of the resulting copolymer. The chemical transformations are shown in Figure 2. Although this material has not been prepared in sufficient quantity for conclusive evaluation as a warp size, some preliminary results have been obtained on the Callaway slasher and the warp-shed tester. Slashing was routine but the results on the warp-shed tester were poor in comparison with those obtained with commercial warp-size-grade PVA. That this material performed at all, however, is an indication that, with proper adjustment of composition and molecular weight, it should be a satisfactory warp size.

Similar considerations apply to another modification of PVA which was prepared recently and found to be precipitated from dilute solution by lowering the pH to about 3. Material costs in a recovery process based on acidification should be low (sulfuric acid: about 1.5¢/lb). This modified PVA was prepared by the copolymerization in emulsion of vinyl acetate, acrylic acid and dibutyl maleate, followed by partial hydrolysis of the resulting copolymer. These transformations are shown in Figure 2.

Results from the warp-shed tester on cotton-polyester (65:35) yarns sized with these copolymers are shown in Table 6.

Removal of Desizing Products of Starch from Desizing Wastes

Starch and the desizing products from starch-sized fabrics are biodegradable and are largely removed from textile-plant wastes by biological treatment systems. Biodegradation, of course, results in the formation of a sludge which must be disposed of by other means. Exploratory attempts were made in the present work to find a procedure for removing starch-desizing products by chemical precipitation.

Examination by thin-layer chromatography (TLC) of enzymatic desizing wastes, from starch-sized fabrics, obtained from a nearby textile plant, showed that none of the low-molecular-weight sugars--dextrose, maltose, maltotriose, etc.--were present. The starch was degraded, of course, but the products were still polymers of relatively high molecular weight. Further enzymatic treatment of the desizing wastes in the laboratory produced the sugars. Similar results were obtained with a desizing waste from another plant which employed a caustic desizing of starch-sized fabrics. If these textile plants are typical, an error has been made by writers who have assumed that starch desizing wastes consist mostly of dextrose and other sugars of relatively low molecular weight.

The above observation suggested that a means might be found for precipitating and recovering starch-desizing wastes as polymers rather than as

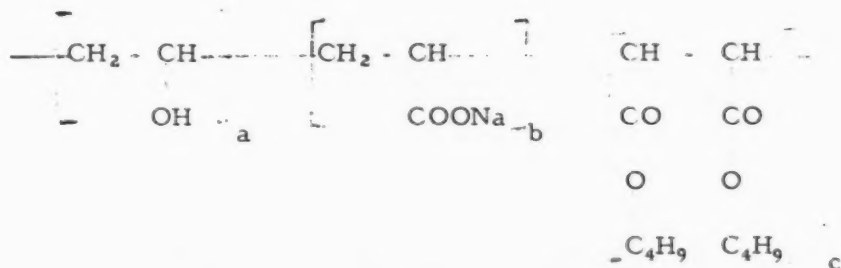
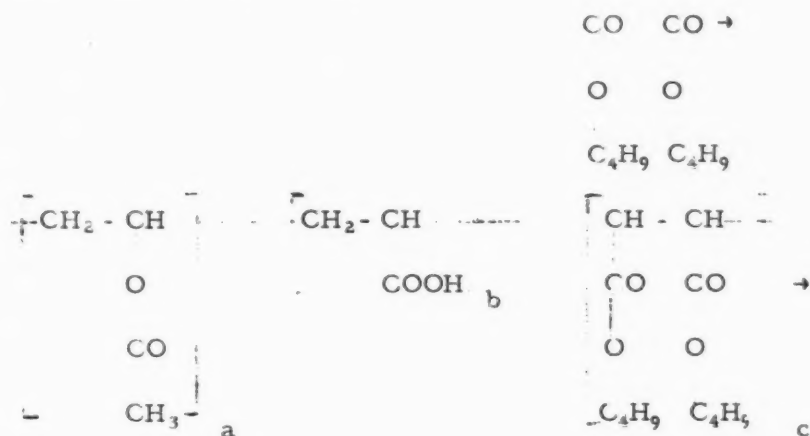
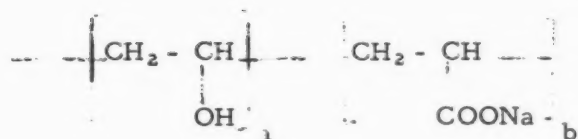
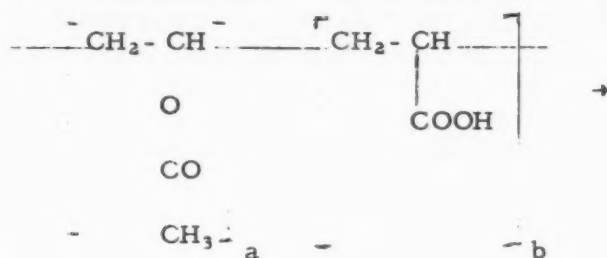
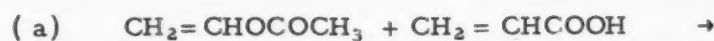


Figure 2. Chemical Transformations in the Preparation of Polyvinyl Alcohol Copolymers

Table 6: Results from Warp-Shed Tester on Yarn Sized with PVA and PVA Copolymers

- a. Vinol 540 polyvinyl alcohol (PVA)
- b. Vinol 125 polyvinyl alcohol (PVA)
- c. Vinyl alcohol/acrylic acid copolymer
- d. Vinyl alcohol/acrylic acid/dibutyl maleate copolymer

Sample	1 ^a	2 ^a	3 ^b	4 ^b	5 ^c	6 ^d
Size add-on (wt %)	12.5	11.7	8.3	8.1	11.5	8.8
Shed (wt %)	0.7	0.8	0.6	0.8	4.1	5.6
Fiber in shed (wt %)	4.6	50	75	75	67	66
Stops	0	0	0	0	5	2
Clinging ratio (%)	25	25	25	25	75	75
Warp tested (yd)	20	20	20	20	12	20
Concn. of size (wt %)	9.8	9.8	8.0	8.0	10.0	7.7

sugar derivatives. The oxidation of starch to give a material containing aldehyde, ketone and carboxylic-acid functions is recorded in numerous publications in the literature and, indeed, "oxidized starch" is a commercial product widely used in the paper industry (12). Oxidation experiments were carried out on starch solutions (1%) to determine if carboxyl groups might be introduced into the starch molecule and permit precipitation with polyvalent metal salts in the same manner as CMC. The oxidizing agents were sodium hypochlorite, a common textile bleach as well as the oxidant used to prepare commercial "oxidized starch"; sodium chlorite, another common textile bleach; and sodium bromite, a starch-desizing agent. None of the oxidations performed so far, however, gave a product which was precipitated with filter alum or ferric chloride. Solutions (1%) of three "oxidized starches" (Stayco G, Stayco M and Stayco S - different viscosity grade of oxidized corn starch from A. E. Staley Manufacturing Co.) were treated with alum but none gave a significant amount of precipitate.

Biodegradation of Carboxymethyl Cellulose (CMC)

In the first exploratory experiment on the biodegradation of CMC, a laboratory aeration chamber (small-scale activated-sludge unit) was arranged for the continuous feed of a dilute (0.03%) solution of CMC containing the necessary mineral nutrients. Bacterial seed was obtained from a municipal sewer. The CMC solution (5 liters) was passed through the aeration chamber (2-liter capacity) and recirculated for four weeks. At the end of this time, a 20% reduction of the CMC content, measured spectrophotometrically (see Appendix A), of the circulating solution was noted. Recirculation was discontinued at this point and the entire mass was transferred to a five-liter flask for aeration in a static condition, a simpler procedure which seemed likely to accomplish the same result as aeration with recirculation. Reduction of CMC content advanced to about 35% and then leveled off. No further reduction occurred even over a prolonged period.

In another experiment, after a suitable sludge (MLSS = 1500 mg/l) had been developed from sewage bacteria and a synthetic sewage feed (see Table 7), the organic materials (dextrose, starch, yeast extract) in the feed were replaced gradually in increments of 10% over a period of 12 weeks with an equivalent amount of CMC (based on COD). The detention time in the aeration chamber was approximately 14 hours. A trend toward reduction of the CMC concentration, measured spectrophotometrically (see Appendix A), between the influent and effluent streams was noted after several weeks and this reduction increased with increasing substitution of the organic matter by CMC. At 100% substitution it was 15% in the beginning and it increased to about 65% after eight weeks. Reductions at this level continued for 10 weeks and then began to decline. The mixed-liquor suspended solids (MLSS) began to decline at the same time, indicating that the system was experiencing a nutritional deficiency. This result was not unexpected since

Table 7. Synthetic Sewage Feed

Ingredients	Amount (mg.)
Yeast extract	158
Dextrose	80
Starch	80
NH ₄ Cl	63
CaCl ₂ · 2H ₂ O	10
FeSO ₄ · 7H ₂ O	10
MnSO ₄ · H ₂ O	10
MgSO ₄ · 7H ₂ O	300
K ₂ HPO ₄	40.3
Tapwater	to 1 liter
COD	300 mg/l

the feed for some time had contained no proteins or vitamins--CMC was the only organic material in the feed. The results of this experiment are shown in Table 8 and in Figures 3 and 4.

For another experiment, a sample of sludge was obtained from a small, experimental aerated lagoon used by Dan River, Inc., Danville, Virginia, in treating a portion of its plant effluents. This plant uses CMC almost exclusively as a warp size and its wastes had been discharged to the lagoon for over two years. The sludge sample (MLSS = 2000 mg/l) was used in a laboratory activated-sludge unit which was fed continuously with a CMC solution (0.03%) containing essential mineral nutrients (see Table 7). A reduction in CMC concentration, measured spectrophotometrically (see Appendix A), between influent and effluent streams was noted almost immediately. This reduction increased and reached the 70-80% level after five weeks and remained in this range for about 10 weeks. At the end of this time it declined precipitously, along with the MLSS, indicating that the system was reacting to a nutritional deficiency. These results are shown in Table 9 and in Figures 5 and 6 .

Biodegradation of Polyvinyl Alcohol (PVA)

After a suitable sludge (MLSS = 1800 mg/l) had been developed in a laboratory activated-sludge unit from sewage bacteria and a synthetic sewage feed (see Table 7), the organic materials (dextrose, starch, yeast extract) in the feed were replaced gradually in increments of 10% over a period of 18 weeks with an equivalent amount of PVA. The detention time in the aeration chamber was approximately two days. A trend toward a reduction of the PVA content, measured spectrophotometrically (see Appendix A), between the influent and effluent streams was noted after four weeks (40% substitution of PVA) and this reduction continued to increase with increasing time and substitution of PVA. It reached approximately 60% after 16 weeks (90% substitution of PVA), remained in the 60-65% range for an additional 17 weeks, and then began to decline--apparently as a result of nutritional deficiency. The results of this experiment are shown in Table 10 and in Figures 7 and 8 .

Table 8: Removal of CMC with Activated Sludge Developed in Laboratory

Date	Time (weeks)	Substitu- tion of CMC (%)	CMC Concentration		Reduction (%)
			Influent (%)	Effluent (%)	
8/14/70	8	70	0.0180	0.0160	11
9/11/70	12	80	0.0210	0.0190	10
9/18/70	13	90	0.0230	0.0210	9
9/23/70	13	100	0.0250	0.0215	14
9/30/70	15	100	0.0295	0.0220	25
10/7/70	16	100	0.0255	0.0210	18
10/14/70	17	100	0.0290	0.0240	17
11/11/70	21	100	0.0280	0.0205	29
11/18/70	22	100	0.0300	0.0110	63
11/25/70	23	100	0.0340	0.0130	62
12/2/70	24	100	0.0330	0.0170	48
12/9/70	25	100	0.0320	0.0120	63
12/16/70	26	100	0.0305	0.0150	52
12/30/70	28	100	0.0280	0.0050	82
1/7/71	29	100	0.0315	0.0085	73
1/15/71	30	100	0.0330	0.0130	61
1/20/71	31	100	0.0310	0.0110	65
2/5/71	33	100	0.0315	0.0200	34
3/11/71	38	100	0.0330	0.0240	27
5/14/71	47	100	0.0295	0.0255	14
5/17/71	47	100	0.0290	0.0240	17

Figure 3 Treatment of CMC with Activated Sludge
Developed in Laboratory

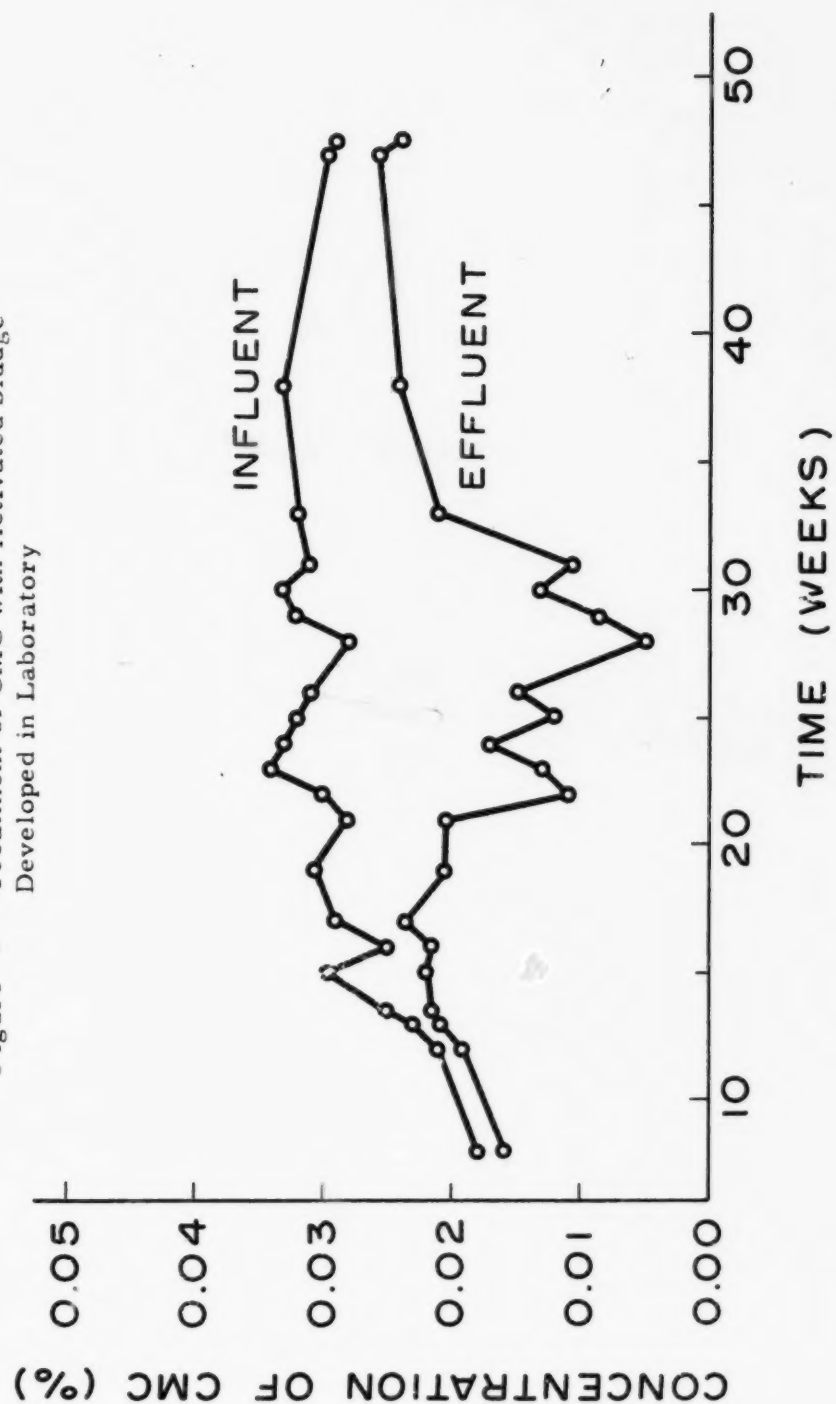


Figure 4: Removal of CMC with Activated Sludge
Developed in Laboratory

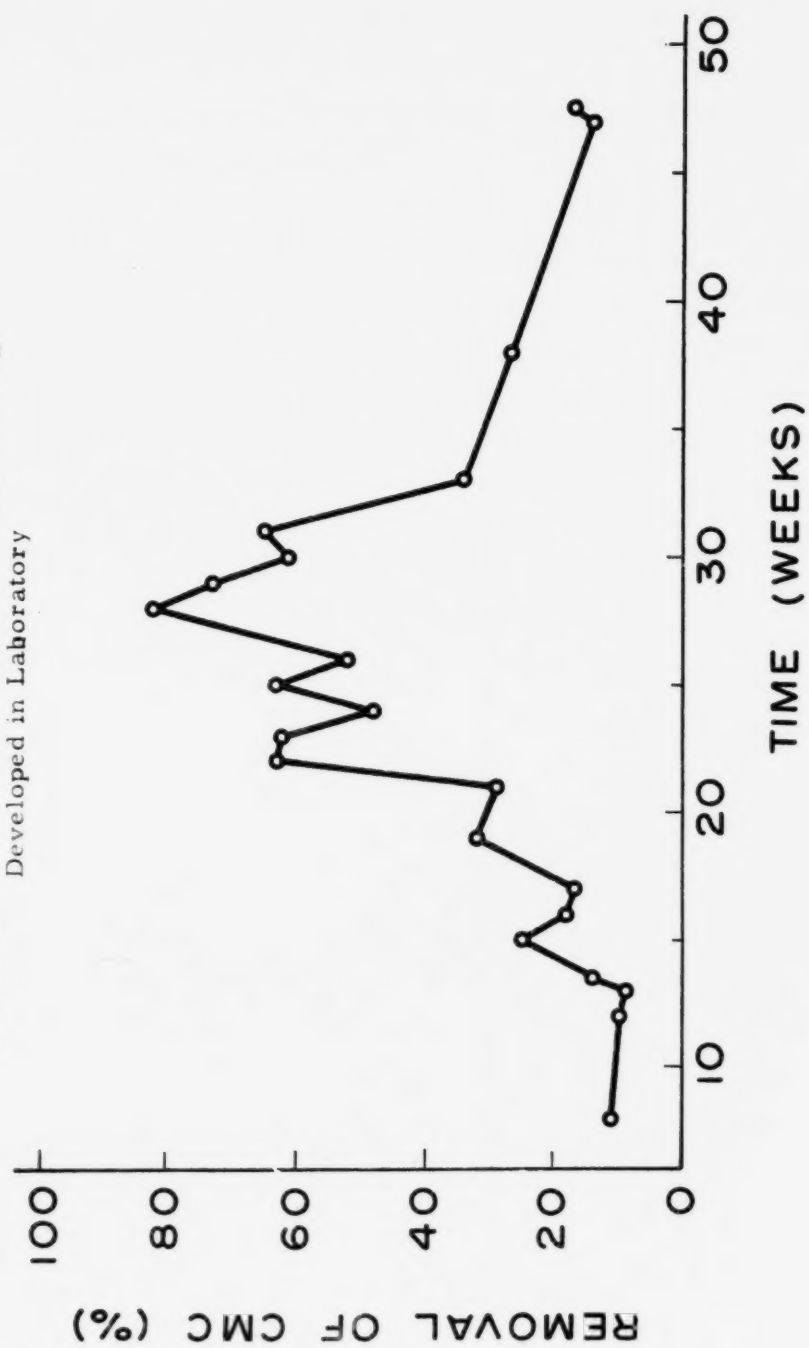


Table 9: Removal of CMC with Activated Sludge from Dan River Treatment Plant

Date	Time (weeks)	CMC Concentration		Reduction (%)
		Influent (%)	Effluent (%)	
9/15/70	0			
9/17/70	2 days	0.027	0.027	0
9/18/70	3 days	0.027	0.024	11
9/23/70	1	0.034	0.015	56
9/30/70	2	0.029	0.015	48
10/7/70	3	0.028	0.016	43
10/12/70	4	0.028	0.012	57
10/21/70	5	0.029	0.009	69
10/28/70	6	0.029	0.009	69
11/4/70	7	0.029	0.010	66
11/11/70	8	0.027	0.005	81
11/18/70	9	0.034	0.006	82
11/25/70	10	0.030	0.007	77
12/2/70	11	0.030	0.006	80
12/9/70	12	0.031	0.007	77
12/16/70	13	0.031	0.011	65
12/30/70	15	0.028	0.024	14
1/6/71	16	0.030	0.028	7
1/15/71	17	0.030	0.029	3
1/20/71	18	0.0275	0.026	5

Figure 5: Treatment of CMC with Activated Sludge from Dan River Treatment Plant

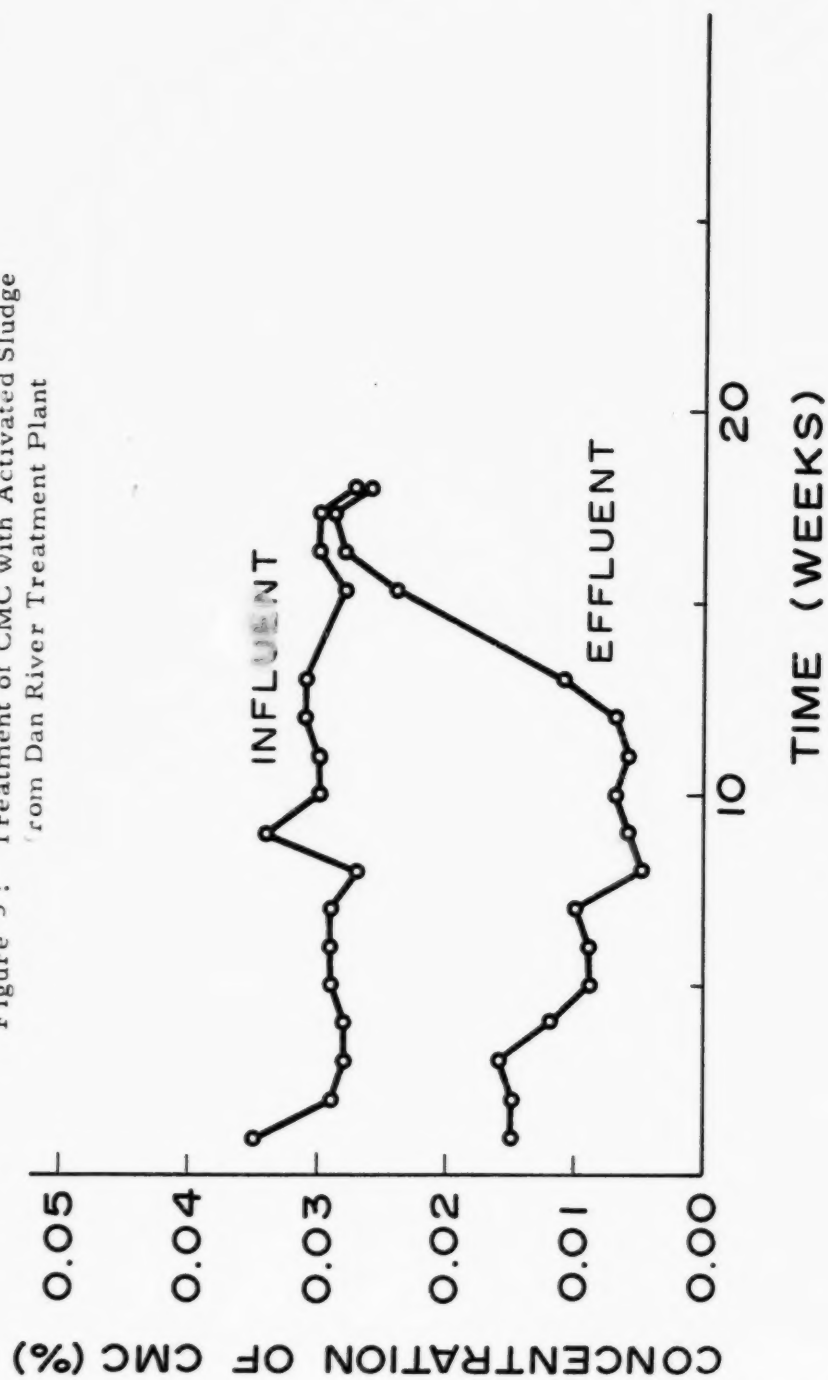


Figure 6: Removal of CMC with Activated Sludge
from Dan River Treatment Plant

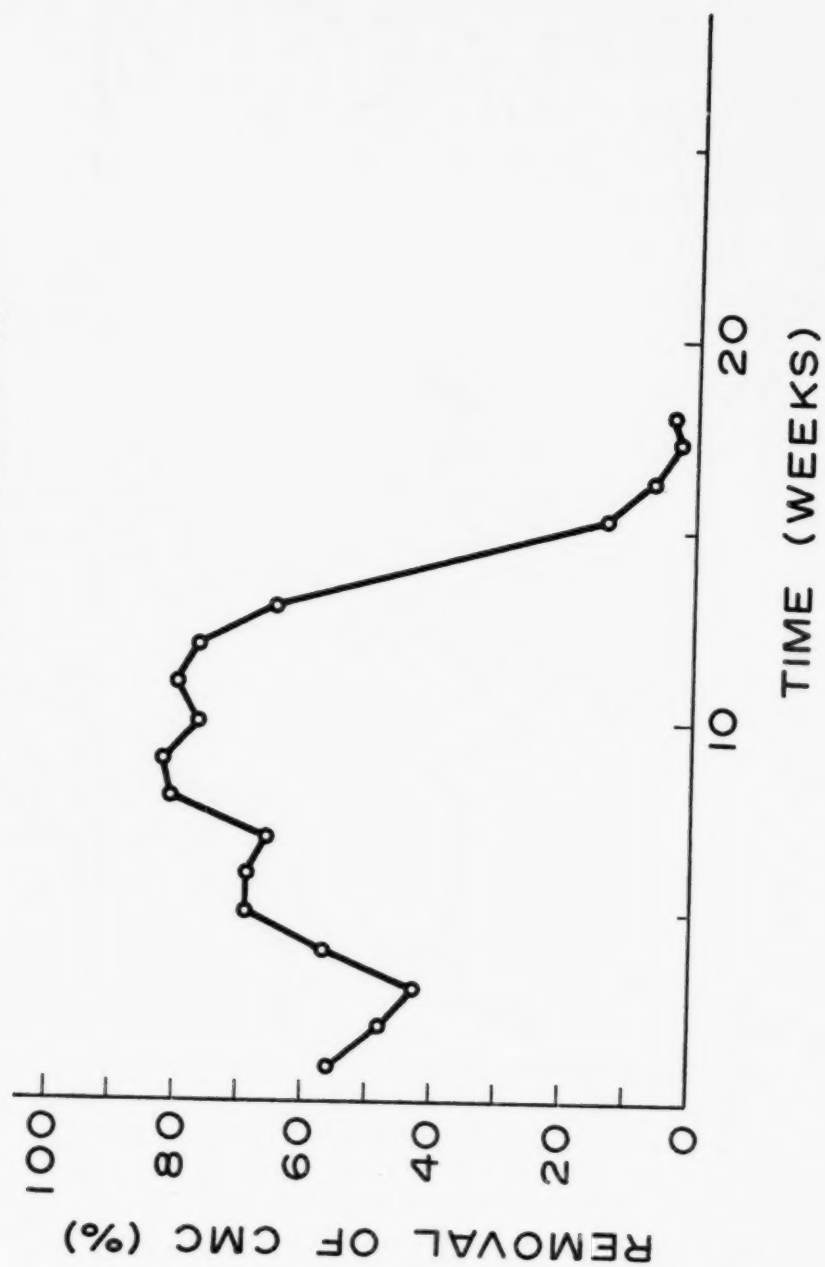


Table 10: Removal of PVA with Activated Sludge Developed in Laboratory

Date	Time (weeks)	Substitu- tion of PVA (%)	PVA Concentration		Reduction (%)
			Influent (%)	Effluent (%)	
9/25/70	0	10			
10/23/70	4	40	0.0125	0.0115	8
12/10/70	11	70	0.020	0.010	50
12/17/70	12	80	0.026	0.006	77
1/6/71	15	80	0.026	0.014	46
1/21/71	17	90	0.026	0.009	65
2/19/71	21	100	0.024	0.010	58
5/14/71	33	100	0.026	0.010	62
5/17/71	33	100	0.026	0.012	54

Figure 7: Treatment of PVA with Activated Sludge
Developed in Laboratory

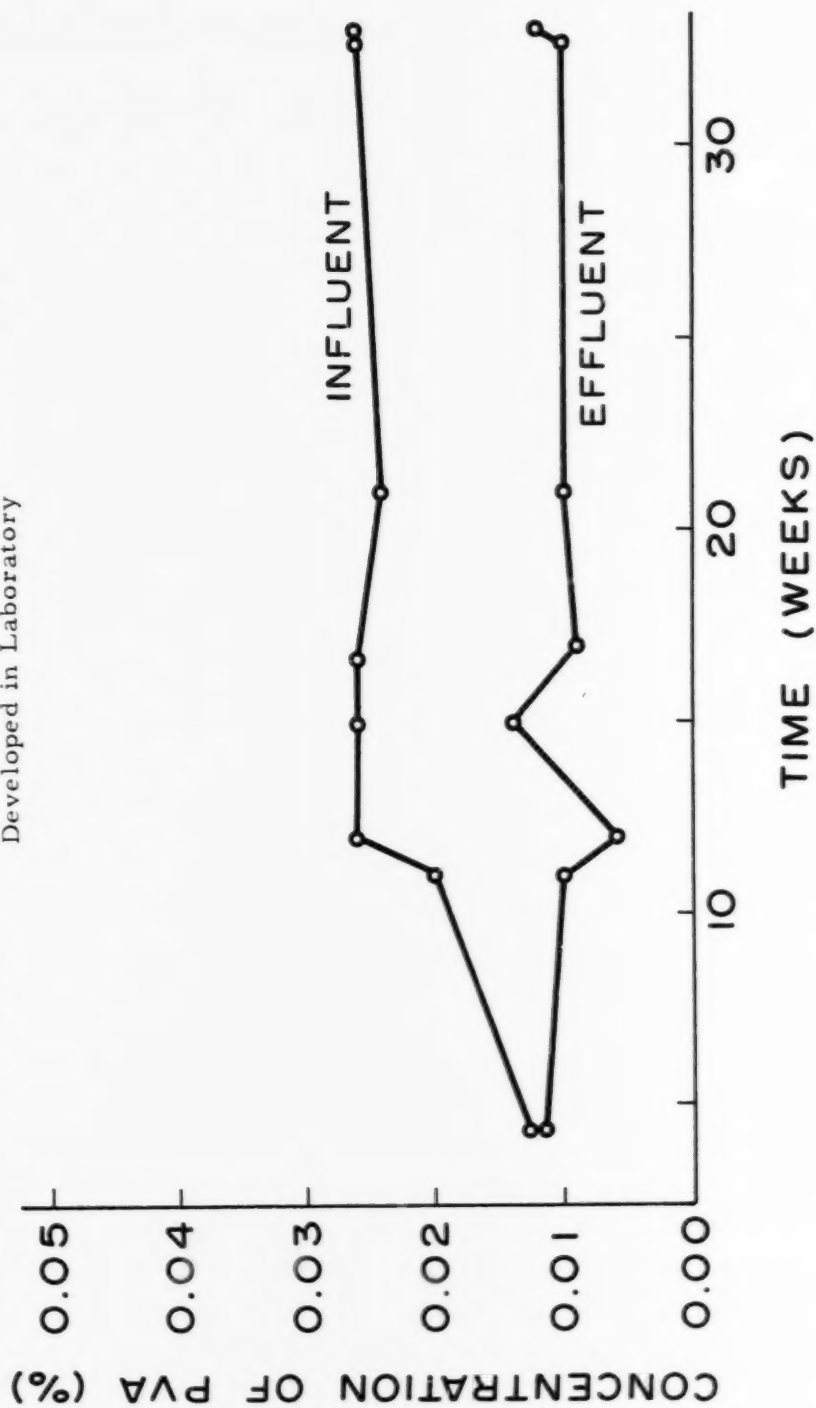
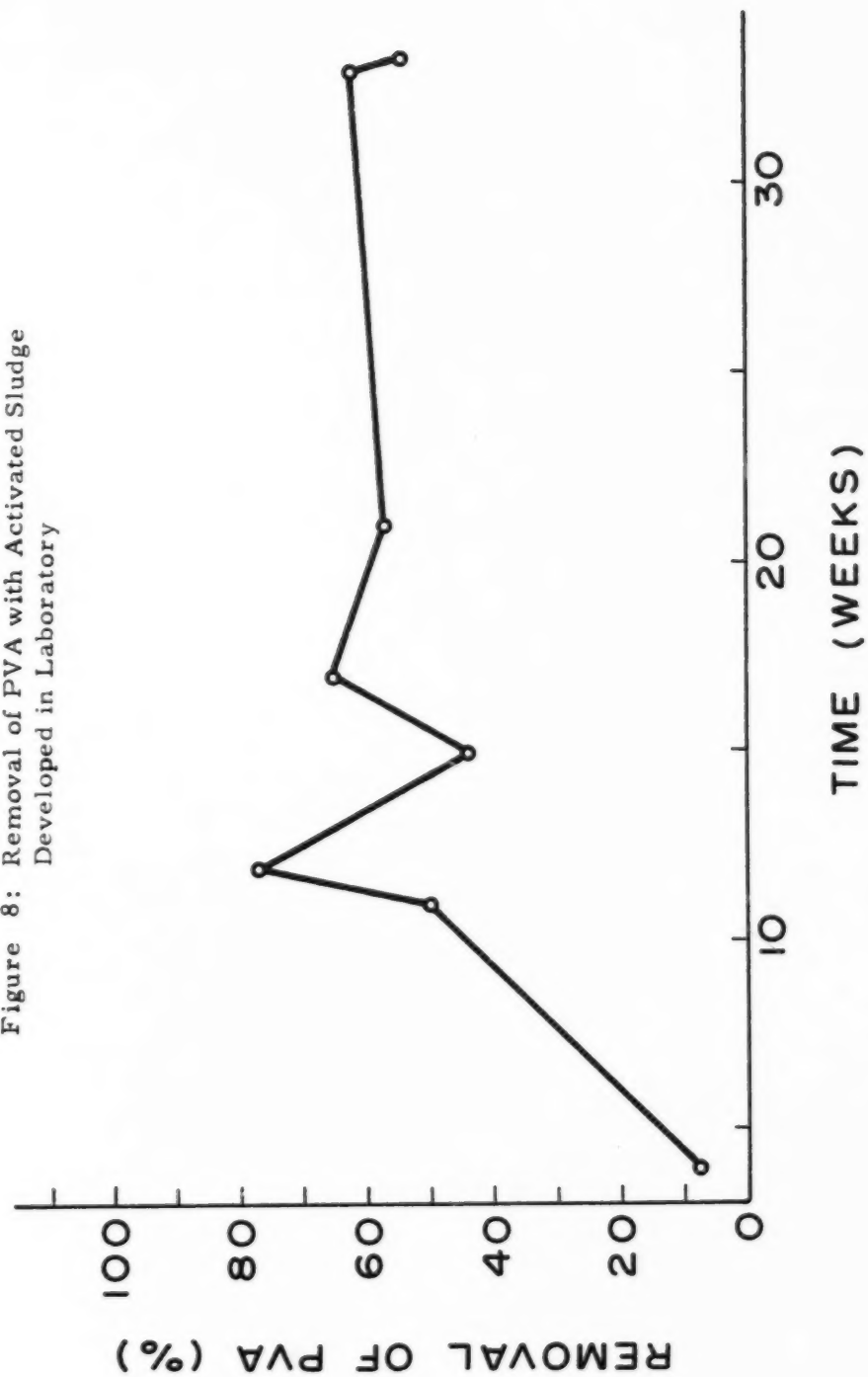


Figure 8: Removal of PVA with Activated Sludge
Developed in Laboratory



SECTION V

ACKNOWLEDGEMENT

This report was prepared by Carl E. Bryan, Project Director, with the assistance of the other people engaged in the work on the project.

The major part of the bench-scale laboratory studies, including the analytical work, was carried out by Peggy S. Harrison. The warp-sizing experiments, together with the trials on the warp-shed tester, were performed by Charles D. Livengood and Gene G. Floyd. The copolymers of vinyl acetate and vinyl alcohol were prepared by Samia G. Saad.

Plant waste samples were obtained through the courtesy of Burlington Industries, Inc., Cone Mills Corporation, and Dan River, Inc.

The interest and advice of Charles Smallwood, Jr., Department of Civil Engineering, throughout the course of this investigation is acknowledged with pleasure. Helpful discussions regarding the biodegradation experiments were held with him and with William S. Galler and Frank J. Humenik, also of the Department of Civil Engineering.

Early phases of the work, including the preparation of the research proposal, were supported by the Water Resources Research Institute of the University of North Carolina, David H. Howells, Director. This support was essential and is hereby acknowledged.

The support of the major part of the program by the Federal Water Pollution Control Administration, later the Environmental Protection Agency, and the help provided by Harold J. Snyder, Jr., the Grant Project Officer, is gratefully acknowledged.

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SECTION VI

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SECTION VII

PUBLICATIONS AND PATENTS

A paper based on a portion of this work was presented before the 20th Southern Water Resources and Pollution Control Conference in Chapel Hill, North Carolina on April 2, 1971 and before a meeting of the Northern Piedmont Section of the American Association of Textile Chemists and Colorists in Durham, North Carolina on April 17, 1971. It is expected that this paper and others resulting from this work will be submitted for publication.

SECTION VIII

APPENDICES

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APPENDIX A - LABORATORY PROCEDURES

Materials

Yarn: A 40/1 cotton-polyester (65:35) yarn was used in the sizing and desizing experiments.

Sodium carboxymethyl cellulose (CMC): A warp-size-grade CMC, labelled cellulose Gum 7L, was obtained from Hercules, Inc.

Polyvinyl alcohol (PVA): Warp-size-grade PVA was obtained from E. I. duPont de Nemours and Co., Inc. (Elvanol 51-05) and Air Reduction Co., Inc. (Vinol 125 and Vinol 540).

Starch: Douglas pearl corn starch from Penick and Ford, Ltd.

Aluminum sulfate (filter alum): Fisher Scientific Co., Technical, No. A-611.

Ferric chloride: Baker and Adamson, Reagent A.C.S., No. 1736.

Other chemicals: The reagents used in the analytical work were of the highest quality available commercially.

Methods

Sizing, Desizing, and Size Recovery

Sizing: The sizing trials were carried out on a Callaway slasher, a laboratory sizing machine, and 252 ends were sized in a single pass.

Desizing: The sized yarns were desized in batches in an autoclave using hot (200-210°F) water. Each batch (about 1700 g) of yarn was treated for 30 minutes with three consecutive portions (each, about 15 liters) of water and, to keep the volume of desizing liquor small, the third portion of water used with each batch of yarn was the first portion used with the next batch. The total solids of the desizing liquors obtained in this way were approximately 1% (10,000 mg/l).

Precipitation of size: A 10% (by weight) solution of filter alum was used in precipitating CMC from desizing wastes, although the concentration of precipitant is not a critical factor. Enough alum was added to effect complete precipitation of the CMC and the amount added was from 75% to 100% of the weight of CMC recovered (See Table 1). The larger ratios of alum to CMC resulted in more rapid coagulation and precipitation with clearer supernatants.

Recovery of precipitated size: The CMC-alum complex settled as a highly swollen, fluffy sludge. Dewatering was accomplished by decanting the supernatant, collecting the swollen sludge on a cloth filter, and then further removing excess water by centrifuging. The amount of water in the sludge was reduced to 90% or less to permit the preparation of a new sizing solution of the proper concentration.

Solution of recovered size: The recovered CMC-alum complex was dissolved in sodium hydroxide for reuse as a warp size. Good agitation was found to be essential for this operation and a laboratory homogenizer (Eppenbach) was used in the present work. The sodium hydroxide (10%) was added dropwise to the stirred sludge and, within a few minutes, a smooth, somewhat cloudy solution with a pH of about 8, was obtained. Adjustment of the concentration was made by the addition of the proper amount of water.

Preparation of polyvinyl alcohol copolymers

Polymerization: Copolymers of vinyl acetate with other monomers were prepared by emulsion polymerization. The reaction was carried out in a multinecked, Pyrex reaction kettle, which was fitted with a mechanical stirrer, a thermometer, a dropping funnel, a reflux condenser and a tube for introducing nitrogen above the reaction mixture. The procedure used in the present work is described in Preparative Methods of Polymer Chemistry (13).

Hydrolysis: The vinyl acetate copolymers, prepared as described above, were hydrolyzed to the corresponding vinyl alcohol copolymers in methanol solution using sodium methoxide as the catalyst. The reaction was conducted in a multinecked reaction flask which was equipped with a mechanical stirrer, a reflux condenser and a dropping funnel. The procedure is described in Preparative Methods of Polymer Chemistry (13).

Oxidation of starch

Oxidation experiments on Douglas pearl corn starch were carried out in Pyrex reaction vessels equipped with a stirrer, thermometer, and a dropping funnel for addition of reagents as needed. Oxidations with sodium hypochlorite were performed at room temperature using up to 20% (by wt, solids basis) sodium hypochlorite, based on starch; oxidations with sodium bromite were performed also at room temperature, with up to 5% (by wt) "Preptone" sodium bromite desizing solution, based on starch; oxidations with sodium chlorite were at 80°C, with up to 10% (by wt) "Textone" sodium chlorite bleach, based on starch. Reactions were allowed to proceed over a period of 4-5 hours or longer, and thinning of the starch occurred in every case, but a significant amount of precipitate was not formed in any case upon addition of alum.

Analyses

Carboxymethyl cellulose (CMC), in desizing liquors and in the effluents from laboratory activated-sludge units, was determined by the 2, 7-dihydroxynaphthalene colorimetric method (3,6). According to this method, the carboxymethyl groups in CMC are converted to glycolic acid by boiling the sample in 50% sulfuric acid. The mixture is then treated with the 2, 7-dihydroxynaphthalene reagent, which reacts with the glycolic acid to give a purple color. The intensity of this color is measured at its absorption maximum of 540 m μ . The principal compounds that interfere are formaldehyde and substances which yield formaldehyde under the conditions of the analysis.

Polyvinyl alcohol (PVA) analysis, in the effluents from laboratory activated-sludge units, was based on the green color produced by the reaction of PVA with iodine in the presence of boric acid (5). The intensity of the color is measured at the absorption maximum of 690m μ . The principal interfering substance likely to be encountered in work of the present nature is starch and its effect can be eliminated by a pre-treatment involving acid hydrolysis.

Aluminum, in CMC-alum complexes and in supernatants, was determined by atomic absorption spectroscopy in accordance with the procedure recommended in the FWPCA manual for chemical analysis (4).

Total solids were determined gravimetrically by the procedure outlined in the FWPCA manual for chemical analysis (4).

Residues at 600°C were determined gravimetrically by the procedure given in Standard Methods (15).

Desizing products from starch-sized fabrics were examined by thin-layer chromatography (TLC). The adsorbent was Kieselguhr G (Merck) impregnated with 0.1 M monosodium phosphate and spread onto glass plates; the solvent was a mixture of n-butanol, n-propanol, acetone, ethyl acetate, ammonium hydroxide (28% NH₃ by wt) and water (7:6:7:4:2:4). The chromatograms were developed by spraying the plates with a solution of potassium dichromate in sulfuric acid and then drying them in an oven. The technique of TLC has been described in a number of monographs; one, edited by Stahl (14), contains a chapter on Sugars and Derivatives which describes analyses of the type carried out in this project.

Biodegradation Experiments

The biodegradation trials on CMC and PVA were carried out in laboratory activated-sludge units, of which two types were used. A picture of one such unit, used in the present work in building up and acclimatizing sludges to CMC and PVA, is shown in Microbiology for Sanitary Engineers by McKinney (8). It is a rectanguloid chamber, 7" (width) x 11" (height) x 13" (length), constructed of polymethyl methacrylate, and divided vertically into four equal compartments, each 7" x 11" x 3", so that four experiments can be conducted simultaneously under the same conditions. The capacity of each compartment is two liters. Provision is made for continuous addition of influent and overflow of effluent, sludge withdrawal, aeration and stirring. A diagramatic sketch of the other unit which was constructed of Pyrex glass is shown in Figure 9. It was used in the trial of CMC biodegradation with a sludge obtained from the waste-treatment plant of a textile mill which had been using CMC as the predominant warp size for several years. The capacity of the aeration chamber is four liters. This unit is designed also for continuous operation.

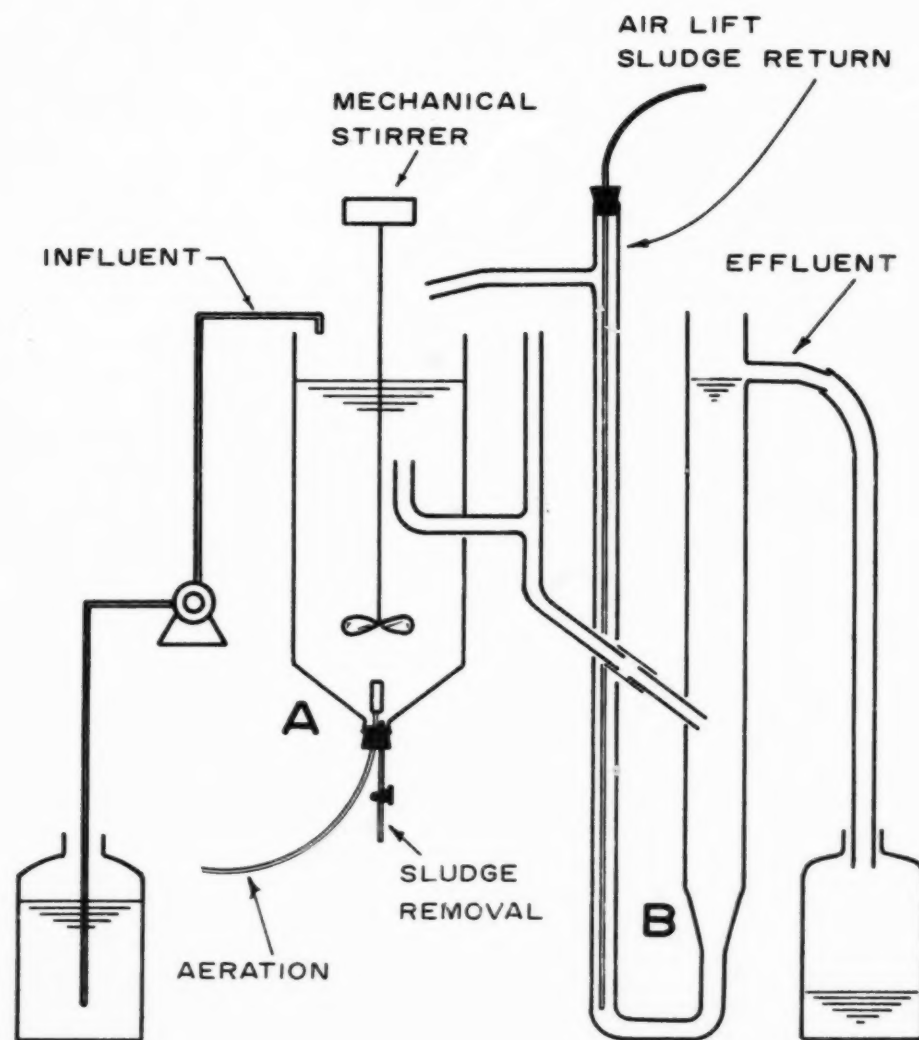


Figure 9: Laboratory Activated-Sludge Unit, Consisting of Aeration Chamber (A) and Separation Basin (B) (approximate scale: two inches = one foot)

APPENDIX B - RELATED LITERATURE

In the Department of Textile Chemistry of the School of Textiles of North Carolina State University, an exploratory study was made of the possibility of recovering and reusing synthetic, or partially synthetic, warp sizes (2) . A large part of this study was a survey of the literature dealing with textile wastes. This survey, which was recently expanded and updated (5) , showed that little work had been done on the recovery and reuse of textile processing chemicals. The caustic soda used in mercerization appears to be the outstanding exception (1, 4, 6) . In the other part of the study at North Carolina State University, it was found that a CMC sizing solution could be reconstituted, by addition of the required amount of CMC to the dilute desizing wastes, to give a formulation which performed satisfactorily as a warp size during weaving.

More closely related to the work described in this report are processes described in three recent patents. According to one patent (3) , an alkali starch phosphate may be used as a warp size for textile yarns; the size is easily removed without degradation after weaving and the desizing liquor, although quite dilute in the examples given, may be used to make up a new starch phosphate, sizing solution. On the other hand, the size may be precipitated from the desizing liquor with a divalent cation, such as calcium, to leave a waste liquor with low BOD. According to the other two patents (7, 8) , alkali metal salts of ethylene-acrylic acid copolymers are suitable for sizing textile yarns and the size is recoverable from the desizing liquors by precipitation with acid. The processes described in these patents, however, do not appear to have received industrial application.

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1	Accession Number	2	Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
			05D	

5	Organization	North Carolina State University Raleigh, North Carolina 27607
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6	Title	Water Pollution Reduction through Recovery of Desizing Wastes
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10	Author(s)	16	Project Designation
	Carl E. Bryan		EPA 12090 EOE 01/72
		21	Note

22	Citation	
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23	Descriptors (Starred First)	Industrial wastes*, Pollution abatement*, Textiles*, Acclimatization*, Chemical precipitation
----	-----------------------------	--

25	Identifiers (Starred First)	Reuse *, Warp sizes *, Carboxymethyl cellulose, Polyvinyl alcohol, Alum
----	-----------------------------	--

27	Abstract	Processes for precipitating from desizing wastes the synthetic warp sizes, carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA), were investigated. Carboxymethyl cellulose is precipitated quantitatively by certain multivalent metal salts, such as aluminum sulfate and ferric chloride. Aluminum sulfate is the more suitable for size recovery. Cycles of sizing, desizing and size recovery were performed on cotton-polyester (65:35) yarns, starting with commercial CMC, and continuing with only the recovered material. After four cycles, the performance of the recovered CMC on a Callaway slasher was satisfactory and results with the sized yarns on a warp-shed tester were equivalent to results with yarns sized with new CMC. Two copolymers of PVA were prepared, one of which was precipitated from dilute solution by aluminum sulfate and ferric chloride, the other by acidification. Preliminary sizing trials with small samples of materials indicate that these, or similar, copolymers may be effective, recoverable warp sizes. Evidence was obtained that acclimatization of sewage bacteria to CMC and PVA occurs upon prolonged contact in a laboratory activated-sludge unit.
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Abstractor	Carl E. Bryan	Institution	North Carolina State University
WR 102 (REV JULY 1969) WRSIC		SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER U.S. DEPARTMENT OF THE INTERIOR WASHINGTON, D. C. 20240	